PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-315785

(43)Date of publication of application : 14.11.2000

(51)Int.Cl. H01L 29/06
B82B 1/00
B82B 3/00
C25D 11/00
G03F 7/00
H01J 1/304
H01J 9/02
// G11B 5/62
G11B 5/84
H01L 43/08

(21)Application number : 11-123594

(22)Date of filing : 30.04.1999

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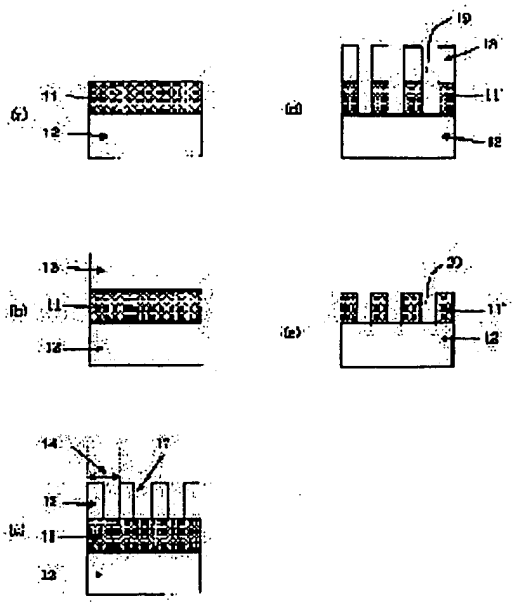
(54) MANUFACTURE OF NANO STRUCTURAL MEMBER AND NANO STRUCTURAL MEMBER DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nano structural member having fine holes which can be used in wide field as functional material for a light emitting device, an optical device, a magnetic device, a micro device, etc.

SOLUTION: In a manufacturing method of a nano structural member where an object to be worked is subjected to anodic oxidation or anodization and fine holes are formed, resist 13 on an object 11 to be worked is interference exposed and developed, part positions 17 penetrating as far as the surface of the object 11 to be worked are formed on the resist 13, and a regular nano structural pattern is formed. After that, the object 11 to be worked is subjected to anodic oxidation or anodization. As a result, a fine whole member having circular fine wholes 20 which are



regularly arranged corresponding to the regular nano structural pattern is formed.

LEGAL STATUS

[Date of request for examination]	12.12.2001
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	withdrawal
[Date of final disposal for application]	11.03.2005
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

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CLAIMS

[Claim(s)]
[Claim 1] A workpiece is set to anodic oxidation or the manufacture approach of the nano structure which carries out anodization and forms pore. The process 1 which forms in this resist the part penetrated to the workpiece front face, and forms a regular nano structure pattern from exposing and developing the resist on a workpiece, Then, the manufacture approach of the nano structure characterized by having the process 2 which forms the pore object which has the pore which carried out the regular array of this workpiece anodic oxidation or by carrying out anodization corresponding to this regular nano structure pattern.
[Claim 2] Said process 1 is the manufacture approach of the nano structure according to claim 1 characterized by being the process which forms a resist on a workpiece, the process which carries out interference exposure of the resist, and the process which forms a regular nano structure pattern according to the process to develop at least.
[Claim 3] Said process 1 is the manufacture approach of the nano structure according to claim 2 characterized by being the process which forms the regular nano structure pattern in which each intersection of an interference fringe carried out the regulation array by having 2 times or more of interference exposure processes, and differing from the direction of an interference fringe in the interference exposure process that the direction of an interference fringe in the 2nd interference exposure process is the 1st time.
[Claim 4] The manufacture approach of the nano structure according to claim 1 to 3 characterized by forming perfect circle pore in the part penetrated to said workpiece front face of the regular nano structure pattern by said resist in said process 2.
[Claim 5] The regular nano structure pattern by said resist is the manufacture approach of the nano structure according to claim 1 to 4 characterized by the width of face of a penetration part being 500nm or less.
[Claim 6] The regular nano structure pattern by said resist is the manufacture approach of the nano structure according to claim 1 to 5 characterized by spacing of each penetration part being 30-1000nm.
[Claim 7] The manufacture approach of the nano structure according to claim 1 to 6 characterized by the part penetrated to said workpiece front face of the regular nano structure pattern by said resist used as a pore formation start point being the repeat of the same spacing and a pattern.
[Claim 8] The manufacture approach of the nano structure according to claim 7 that said pore formation start point is characterized by being the repeat of a forward 6 square-shape-like pattern.
[Claim 9] The manufacture approach of the nano structure according to claim 7 that said pore formation start point is characterized by being the repeat of a 4 square-shape-like pattern.
[Claim 10] The manufacture approach of the nano structure according to claim 1 to 9 characterized by being the bulk to which said workpiece uses aluminum as a principal component.
[Claim 11] The manufacture approach of the nano structure according to claim 1 to 9 characterized by being a forming [said workpiece]-on base-film which uses aluminum as principal component thing.
[Claim 12] The manufacture approach of the nano structure according to claim 1 to 9 characterized by

being the bulk to which said workpiece uses Si as a principal component.
[Claim 13] The manufacture approach of the nano structure according to claim 1 to 9 characterized by being a forming [said workpiece]-on base-film which uses Si as principal component thing.
[Claim 14] The nano structure manufactured by the approach according to claim 1 to 13.
[Claim 15] The manufacture approach of the nano structure using the nano structure according to claim 14 as mold or a mask.
[Claim 16] The nano structure manufactured by the approach according to claim 15.
[Claim 17] The electron emission component characterized by having the electron emission section in the pore of a base with the regular nano structure in the nano structure according to claim 16.
[Claim 18] The photograph nick device which has the structure which embedded the matter with which a base differs from a dielectric constant in the pore of a base with the regular nano structure in the nano structure according to claim 16, and is characterized by an optical distribution property and optical propagation being controllable.
[Claim 19] The magnetic device characterized by embedding the magnetic substance in the pore of a base with the regular nano structure in the nano structure according to claim 16.
[Claim 20] The luminescence device characterized by embedding an illuminant in the pore of a base with the regular nano structure in the nano structure according to claim 16.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nano structure device using the manufacture approach of the nano structure which attained regulation-ization of the nano structure and the regular nano structure by the regular nano structure pattern on the workpiece which used interference exposure as mold or a mask.
[0002]
[Description of the Prior Art] In a metal and the thin film of a semi-conductor, a thin line, and a dot, there is a unique thing for which electric, optical, and chemical property are shown by shutting up a motion of an electron in size smaller than a certain characteristic die length. The interest about the ingredient (nano structure) which has structure more detailed than several 100nm as high-performance material from such a viewpoint is increasing. As the production approach of such the nano structure, photolithography is begun and the approach of producing the nano structure directly with semi-conductor processing techniques including detailed pattern formation techniques, such as electron beam lithography and X-ray lithography, is mentioned, for example. There is the approach of producing the periodic nano structure for a large area and a short time also in photolithography, especially using 2 flux-of-light interference exposure. This approach has the description which can produce the periodic nano structure pattern to the one half period of operating wavelength. The formation approach of this detailed pattern is reported, for example (Optical Engineering 1976 Vol.15 No.3, J.Vac.Sci.Technol.B15 (6), Nov/Dec1997).
[0003] Moreover, the attempt which is going to realize the new nano structure is in the base in the regular structure formed automatically, i.e., the structure formed in a self-regulation target, besides such a production approach. Since such technique may be able to produce the detailed and special structure which turns around the conventional approach a top depending on the fine structure used as the base, many researches are beginning to be done.
[0004] The anodic oxidation which can produce easily the nano structure which has the pore of nano size with sufficient control as such self-regular technique is mentioned. For example, the anodic oxidation alumina which produces aluminum and its alloy by anodizing in an acid bath is known.
[0005] If aluminum plate is anodized in an acid electrolyte, a porosity oxide film will be formed (for example, reference, such as R.C.Furneaux and W.R.Rigby&A.P.Davidson NATURE Vol.337 P147 (1989)). The very detailed cylindrical pore (nano hole) whose diameter is several nm - hundreds of nm has the description of this porosity oxide film in having the specific geometric structure of arranging in parallel at intervals of several nm - hundreds of nm (cell size). The pore of the shape of this cylinder has a high aspect ratio, and is excellent also in the uniformity of the path of a cross section. Moreover, when the path and spacing of this pore adjust the current in the case of anodic oxidation, and an electrical potential difference, the thickness of an oxide film and the depth of pore are controlling the time amount of anodic oxidation, and a certain amount of control is possible for them.
[0006] Moreover, in order to improve the perpendicularity, the linearity, and the independence of pore

of a porosity oxide film Once removing the approach, i.e., the porosity oxide film which formed by performing anodic oxidation, of performing two steps of anodic oxidation, it anodizes again. Better perpendicularity, linearity, The approach of producing the porosity oxide film which has the pore which shows an independence is proposed (Jpn.Journal of Applied Physics, Vol.35, Part2, No.1B, pp.L126-L129, 15 January1996). Here, this approach uses that the hollow of the front face of aluminum plate made when removing the anodic oxide film formed by the first anodic oxidation serves as a pore formation start point of the 2nd anodic oxidation.

[0007] In order to improve the controllability of the configuration of the pore of a porosity oxide film, spacing, and a pattern furthermore It anodizes, after forming the hollow which forces on the front face of aluminum plate the approach of forming a pore formation start point using a stamper, i.e., the substrate which equipped the front face with two or more projections, and can do it as a pore formation start point. The approach of producing the porosity oxide film which has the pore which shows the controllability of a better configuration, spacing, and a pattern is also proposed (JP,10-121292,A).

[0008] Various application which paid its attention to the specific geometrical structure of this anodic oxidation alumina is tried. Although the description by Masuda is detailed, the application is listed hereafter.

[0009] For example, the application and the coat as a coat using the abrasion resistance of an oxide film on anode and insulation-proof are exfoliated, and there is application of fill TAHE. Furthermore, various application which makes the start coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, an optical element, a solar battery, and a gas sensor is tried from using the technique filled up with a metal, a semi-conductor, etc. in a nano hole, and the replica technique of a nano hole. Furthermore, the application to the directions of many, such as the quantum effectiveness devices, such as quantum wire and an MIM component, and a molecule sensor using a nano hole as a chemical reaction place, is expected. (The Masuda solid-state physics 31,493 (1996))

[0010]

[Problem(s) to be Solved by the Invention] Production of the direct nano structure by the semi-conductor processing technique expressed previously has problems, like the badness of the yield and the cost of equipment are high, and technique producible with sufficient repeatability by simple technique is desired.

[0011] About interference exposure, since an interference wave is a sine wave, a high aspect ratio pattern cannot be minced to a resist. Moreover, a crossover include angle is changed, 2nd interference exposure is performed, and producing mesh-like puncturing is also performed. In this case, it was difficult to make the configuration of an aperture into a perfect circle.

[0012] It is wished from it being possible for the self-regular technique, especially the technique of anodic oxidation to be able to produce the nano structure with sufficient control easily from such a viewpoint, and to produce the nano structure of a large area.

[0013] However, although many techniques in which the pore object produced only by the usual anodic oxidation controlled the configuration of the pore and a pattern were developed, there was a limitation in the control. As control in an anodic oxidation alumina, the thing controllable to some extent is known [depth / of pore / pore size] for time amount in pore spacing on the anodic oxidation electrical potential difference at pore wide processing.

[0014] Furthermore, the example which the regulation-ized nano hole which perfect circle pore arranged in the shape of a honeycomb by anodizing under suitable anodic oxidation conditions by Masuda and others as an example which controlled the array of pore produced is reported. However, in this regulation-ized nano hole, there were technical problems, like there is a limit to be anodized [of long duration] in pore spacing of the pore object which can be produced.

[0015] Moreover, in the approach of performing two steps of anodic oxidation, although the perpendicularity, the rectilinear-propagation nature, and the independence of pore of a porosity oxide film have improved, since turbulence arose to the pattern of pore, the configuration and spacing of pore were not fixed, but had the technical problem that these controllabilities were not good.

[0016] In the approach of furthermore forming a pore formation start point using a stamper, the

controllability of the configuration of the pore of a porosity oxide film, spacing, and a pattern had the technical problem which is described below, although improved.
(1) Since the stamper is used, it is difficult to form a pore formation start point in a front face to an irregular workpiece at homogeneity.
(2) Since there is risk of a workpiece being destroyed to the workpiece whose mechanical strength is not strong since it is necessary to put a pressure on a workpiece at the time of stamper use, application is difficult.
(3) Since it is difficult to expose aluminum on a front face to a workpiece by which the film was formed in aluminum front face since compression by the stamper is used, it is difficult to make a stamp location into a pore formation start point.
(4) It is not easy to have to use a hydraulic press at the time of use of a stamper, and to position a pattern with high precision.
(5) It is not easy for production of a stamper to produce without a defect the stamper which must use ultra-fine processing technology time-consuming [like electron beam lithography], and has the projection of uniform high density for a short time.
[0017] The purpose of this invention is to solve these technical problems. That is, the purpose of this invention is offering the technique which can be manufactured in cheap, easy, and a short time over a large area for the pore of the shape of a perfect circle arranged to the arbitration period in the nano structure which has the pore produced by anodic oxidation or anodization.
[0018] It is offering the new nano structure which the purpose of this invention uses as the base the nano structure which has the pore produced with the application of this manufacturing technology, and can be applied in various directions, and a nano structure device furthermore.
[0019]
[Means for Solving the Problem] The configuration of this invention accomplished that the above-mentioned purpose should be attained is as follows.
[0020] Namely, the 1st sets the workpiece of this invention to anodic oxidation or the manufacture approach of the nano structure which carries out anodization and forms pore. The process 1 which forms in this resist the part penetrated to the workpiece front face, and forms a regular nano structure pattern from exposing and developing the resist on a workpiece, Then, it is related with the manufacture approach of the nano structure characterized by having the process 2 which forms the pore object which has the pore which carried out the regular array of this workpiece anodic oxidation or by carrying out anodization corresponding to this regular nano structure pattern.
[0021] the 1st manufacture approach of this invention -- as the further description -- "-- said process 1 The process which forms a resist on a workpiece at least, and the process which carries out interference exposure of the resist, What [is been the process which forms a regular nano structure pattern according to the process to develop"] "said process 1 By having 2 times or more of interference exposure processes, and differing from the direction of an interference fringe in the interference exposure process that the direction of an interference fringe in the 2nd interference exposure process is the 1st time "What [each intersection of an interference fringe is the process which forms the regular nano structure pattern which carried out the regulation array"] In said process 2 What [perfect circle pore is formed in the part penetrated to said workpiece front face of the regular nano structure pattern by said resist for"] "the regular nano structure pattern by said resist What [the width of face of a penetration part is 500nm or less"] "the regular nano structure pattern by said resist What spacing of each penetration part is 30-1000nm", the thing "which the part penetrated to said workpiece front face of the regular nano structure pattern by said resist used as a pore formation start point is the repeat of the same spacing and a pattern", What "said pore formation start point is the repeat of a forward 6 square-shape-like pattern", What "said pore formation start point is the repeat of a 4 square-shape-like pattern", What "said workpiece is the bulk which uses aluminum as a principal component", the thing "which said workpiece is a forming-on base-film which uses aluminum as principal component thing", What "said workpiece is the bulk which uses Si as a principal component", and the thing "which said workpiece is a forming-on base-film which uses Si as principal component thing" are included.

[0022] The 2nd of this invention is related with the nano structure manufactured by the 1st approach of above-mentioned this invention.
[0023] The 3rd of this invention is related with the manufacture approach of the nano structure which uses the 2nd nano structure of above-mentioned this invention as mold or a mask.
[0024] The 4th of this invention is related with the nano structure manufactured by the 3rd approach of above-mentioned this invention.
[0025] The 5th of this invention is related with the electron emission component characterized by having the electron emission section in the pore of a base with the regular nano structure in the 4th nano structure of above-mentioned this invention.
[0026] The 6th of this invention has the structure which embedded the matter with which a base differs from a dielectric constant in the pore of a base with the regular nano structure in the 4th nano structure of above-mentioned this invention, and is related with the photograph nick device characterized by an optical distribution property and optical propagation being controllable.
[0027] The 7th of this invention is related with the magnetic device characterized by embedding the magnetic substance in the pore of a base with the regular nano structure in the 4th nano structure of above-mentioned this invention.
[0028] The 8th of this invention is related with the luminescence device characterized by embedding an illuminant in the pore of a base with the regular nano structure in the 4th nano structure of above-mentioned this invention.
[0029]
[Function] According to the manufacture approach of the nano structure of this invention, in the nano structure which has the pore produced by anodic oxidation or anodization, the pore of the shape of a regular perfect circle can be formed over a large area by combining the property of the regular nano structure pattern of a resist and the formation of a self-regulation which were formed on the workpiece.
[0030] Namely, although the interference exposure itself suitably used by this invention cannot mince a high aspect ratio pattern to a resist since an interference wave is a sine wave, as for anodic oxidation, a pore diameter grows by the shape of a perfect circle. Moreover, the regulation-ized pore array of a regular nano structure pattern and an anodic oxidation alumina can be fitted by performing interference exposure of a resist twice (coincidence). for this reason -- if the regular nano structure pattern by interference exposure of a resist is used as an anodic oxidation mask, even if the configuration of the penetration part of this regular nano structure pattern is not a perfect circle -- high -- the aspect nano structure is producible.
[0031] Since the manufacture approach of the nano structure of this invention uses the regular nano structure pattern by the resist as a mask of a workpiece, it does not need to form a pore formation start point in a workpiece front face, and does not exfoliate a resist, but can perform anodization and anodic oxidation succeedingly.
[0032] The manufacture approach of the nano structure of this invention needs to use neither two anodic oxidation nor a stamper compared with the conventional anodic oxidation regulation-ized nano hole creating method. Therefore, while the thickness of a workpiece is called for correctly, when forming a pore formation start point, it is not necessary to put a pressure on a workpiece, and a mechanical strength can apply also to the workpiece which is not strong.
[0033] The manufacture approach of the nano structure of this invention is practical at the point which does not damage a large area, low cost, and a workpiece front face far for a short time, but can produce the periodic nano structure rather than it forms each pore formation start point in a workpiece front face using semi-conductor processing techniques, such as electron beam lithography.
[0034] Since it is possible to expose aluminum on a front face also to a workpiece by which the film was formed in aluminum front face if it is less than the thickness (difference of elevation) of a nano structure pattern since the regular nano structure pattern is used for formation of a pore formation start point, the manufacture approach of the nano structure of this invention can form a pore formation start point.
[0035] Since the manufacture approach of the nano structure of this invention uses the regular nano structure pattern of the resist formed on the workpiece as an anodic oxidation mask, it does not need to

position a pattern and large-area-izing and regulation-izing are easy for it.
[0036] Since the manufacture approach of the nano structure of this invention uses the regular nano structure pattern of the resist formed on the workpiece as an anodic oxidation mask, only depending on the penetration part of this regular nano structure pattern, random-arrangement-izing of pore is still more possible for a pore formation start point.
[0037] The nano structure of this invention can be used as the base material of the further new nano structure, mold, etc., although it is usable as a functional material in itself. Specifically, it is applicable with new electronic DEBAISUHE by embedding functional materials, such as a metal and a semi-conductor, at the pore of the nano structure of this invention.
[0038] Furthermore, the nano structure of this invention makes it possible to apply optical elements including quantum wire, an MIM component, a molecule sensor, coloring, a magnetic-recording medium, EL light emitting device, an electrochromic element, and a photograph nick band, an electron emission component, a solar battery, a gas sensor, abrasion resistance, the insulation-proof sex skin film, and a filter with various gestalten made into the start, and has the operation which extends the application range remarkably.
[0039]
[The mode of implementation of invention] Hereafter, the example of an embodiment of the manufacture approach of the nano structure of this invention is explained with reference to drawing 1 and drawing 2 . Following process (a) - (f) corresponds to (a) - (f) of drawing 1 and drawing 2 R> 2, respectively.
[0040] (a) Prepare a workpiece preparation workpiece. Although what uses aluminum as a principal component is mentioned as the quality of the material of the workpiece of this invention, if it is the quality of the material in which the pore formation by anodic oxidation is possible, it will not be limited especially.
[0041] The bulk 10 which uses as a principal component aluminum shown in drawing 1 (a-1) as an example of the 1st gestalt of the workpiece of this invention is mentioned. Moreover, although it is not necessarily required to perform mirror-polishing processing in the bulk which uses aluminum as a principal component in order to give smooth nature to a front face, it is more desirable for there to be no surface irregularity, since periodic nano structure is produced on a workpiece.
[0042] Next, what formed the film 11 which uses aluminum as a principal component as an example of the 2nd gestalt of the workpiece of this invention on the base 12 shown in drawing 1 (a-2) is mentioned. At this time, as a base 12, although the thing in which the film of one or more layers was formed on substrates, such as insulator substrates and silicon including quartz glass, and semi-conductor substrates including gallium arsenide, and these substrates is mentioned, if there is no un-arranging in the pore formation by anodic oxidation of the film 11 which uses aluminum as a principal component, the quality of the material of a base 12, thickness, especially a mechanical strength, etc. will not be limited. For example, if what formed the film of pore formation terminal point members, such as Ti and Nb, on the substrate as a base 12 is used, it will also become possible to raise the homogeneity of the depth of pore.
[0043] Moreover, as for the membrane formation approach of the film 11 which carries out a principal component, the membrane formation approach of arbitration including resistance heating vacuum evaporationo, EB vacuum evaporationo, a spatter, CVD, and plating can apply aluminum. In the film 11 which uses aluminum as a principal component, the forming-membranes method which the surface irregularity resulting from existence of a grain etc. does not generate as much as possible is desirable.
[0044] (b) Apply a resist 13 to the resist spreading above-mentioned workpiece to a workpiece top (drawing 1 (b-1)). the processed front face dries every [each / 10] beforehand in an acetone and IPA in clean ultrasonic-cleaning and 20-120 minute or more oven.
[0045] Both the high resolution positive resist corresponding to i line and the high resolution negative resist corresponding to i line of a use resist are usable. The thing corresponding to a positive type and each negative mold is used for a developer in that case. The AZ5214E positive resist made from Clariant JAPAN was thinned and used with resist thinner liquid this time.
[0046] before resist spreading -- HMDS spreading and an antireflection film 15 -- either is applied

(drawing 1 (b-2)). HMDS used this time used AZBARLi100 of the product [antireflection film / 15] made from Clariant JAPAN using the object by Chisso Corp. In case HMDS applies a resist, it raises resist **** to a coated material top chemically. The antireflection film 15 is effective in order the reflection factor of a workpiece is high, or to suppress the interference in the film and to reduce unevenness of exposure. However, in case the antireflection film 15 is used as a substrate of a resist, in order to deposit a workpiece front face after resist exposure / development, there is the need for dry etching.

[0047] HMDS spreading, antireflection-film spreading, and resist spreading are performed by the SUPINKO toner method. After putting a workpiece on a stage and making a front face into clarification by nitrogen blow, it applies changing a rotational frequency gradually like initial velocity, ****, final velocity, and slope. Thus, by applying, it can apply and unevenness can be reduced. Then, desiccation processing is performed using a hot plate or clean oven.

[0048] (c) By performing interference exposure of the 1st interference exposure [1st], a resist 13 exposes in the shape of [of period 14] a stripe, and the sensitization section 16 is formed (refer to drawing 1 (c-1) of a substrate sectional view, and drawing 1 of a substrate surface Fig. (c-2)).

[0049] The interference aligner used this time is AOI. SANSHO FX4010 made from CO. and Ltd was used. helium-Cd laser (wavelength of 325nm, TEM00 mode) was used for laser. Since interference exposure can mince a pattern to the half-wave length period of wavelength theoretically, especially the class of laser to be used is not asked. However, the laser quality of the stable output and the TEM00 stable mode is desirable.

[0050] Moreover, since it exposes using interference of light, it is necessary to stop covering equipment in an acrylic case, and air-conditioning, and to make fluctuation of air into the minimum. Moreover, in order to lose the shake by equipment itself, it is made vibrationproofing base structure. In order to keep interference reinforcement constant, it is necessary to adjust each optical path using a power meter, the sensitization version, etc. in the case of an experiment, and to check an interference fringe at it.

[0051] As mentioned above, interference exposure needs precise adjustment and its repeatability is not so good on the occasion of exposure and development. Therefore, fluctuation of some mixes in exposure / development conditions by resist coating unevenness, unevenness of exposure, the difference in a sample, and the development temperature gradient.

[0052] (d) As by making the direction of an interference fringe of the 1st time intersect (for example, 60 degrees, a 90-degree crossover) shows interference exposure of the 2nd development to drawing 2 (d-2) after the 2nd interference exposure, the intersection part 17 by the interference fringes of the different direction is formed. This part 17 exposed strongly develops negatives so that a part for a crevice may be formed. In addition, spacing 18 shows spacing for the formed crevice.

[0053] Since there is an inclination for the pattern of pore to become the repeat of a forward hexagon-like pattern mostly by self-organizing in the pore formation by anodic oxidation at this time, forming so that the regular nano structure pattern (pattern for the crevice 17 which even the aluminum film 11 penetrated) used as an anodic oxidation mask may become the repeat of a forward hexagon-like pattern mostly makes sense. This is desirable especially when it is going to form the nano structure which has deep pore. However, since the above-mentioned self-organizing does not happen yet when pore is shallow, also in forming so that the regular nano structure pattern which has a part for a crevice 17 may become the repeat of the pattern of configurations of arbitration, such as the shape of a square, mostly, semantics comes out. When this forms the film with which a workpiece uses aluminum as a principal component on a base, since the depth of pore becomes shallow inevitably, it becomes significant especially.

[0054] Moreover, in the pore formation by anodic oxidation, spacing of pore is controllable by process terms and conditions, such as the class of electrolytic solution used for anodic oxidation, concentration, temperature and the anodic oxidation electrical-potential-difference impression approach, an electrical-potential-difference value, and time amount, to some extent. Therefore, forming the regular nano structure pattern which has a part for a crevice 17 beforehand in spacing of the pore expected from process terms and conditions makes sense.

[0055] (e) Use as a mask the regular nano structure pattern which consists of a resist 13 in which the anodization above-mentioned crevice 17 was formed, and produce the nano structure which has the perfect circle-like pore 19 in a workpiece by performing anodizing to the above-mentioned workpiece.
[0056] In the electrolytic solution used for anodic oxidation, although oxalic acid, phosphoric acid, a sulfuric acid, a chromic-acid solution, etc. are mentioned, especially if there is no un-arranging in the pore formation by anodic oxidation, it will not be limited. Moreover, terms and conditions according to each electrolytic solution, such as an anodic oxidation electrical potential difference and temperature, can be suitably set up according to the nano structure to produce.
[0057] (f) After exfoliating the resist 13 of a resist exfoliation above-mentioned regular nano structure pattern with resist exfoliation liquid, pore size can be suitably extended by **** pore wide processing in an acid solution (the case of an anodic oxidation alumina for example, phosphoric-acid solution). It can consider as the nano structure which has the pore 20 of a desired path with acid concentration, the processing time, temperature, etc. the last and ultrapure water -- a stream -- it washes.
[0058]
[Example] Hereafter, the example of this invention is explained.
[0059] (Example 1) In the production approach of the nano structure which anodizes aluminum film vapor-deposited on the substrate, and forms pore, this example formed the regular nano structure pattern by performing one interference exposure to the resist formed on aluminum film, and this was used for it as an anodization mask. Hereafter, the production approach of the nano structure of this example is explained using drawing 3 .
[0060] (1) On the n-Si substrate 12, the aluminum film 11 (500nm of thickness) was formed (drawing 3 (a)).
[0061] (2) Next, the resist film 13 (200nm of thickness) was applied and dried with the spin coat method after an acetone, washing by IPA, and desiccation (drawing 3 R> 3 (b)). (90-degree 20 minutes)
[0062] (3) Next, produce the regular nano structure pattern by the resist with periodic stripe-like structure (spacing 14 is 230nm) using interference exposure. In this example, helium-Cd laser (lambda= 325nm, 230nm spacing of interference fringes) is used, and it is exposure 29.5 mJ/cm2. It exposed. And the developer was diluted with pure water to 1 to 1, and the regular nano structure pattern which has the crevice 17 of the shape of a stripe penetrated up to aluminum film 11 front face in developing negatives about 30 seconds was formed for 90 seconds (drawing 3 (c)). Drawing 4 is the top view of this regular nano structure pattern.
[0063] (4) Next, the pore 19 periodically arranged on the aluminum film 11 (alumina film 11') was formed by anodizing by phosphoric-acid 0.3M solution and 100V (drawing 3 R> 3 (d)).
[0064] (5) Finally, resist exfoliation liquid was used, the resist 13 was removed from the processed substrate, it was immersed in the 5wt% phosphoric acid for 30 minutes, and puncturing processing (pore wide processing) was performed (drawing 3 (e)).
[0065] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, as shown in drawing 5 , corresponding to the crevice 17 of the interference fringe of 230nm spacing, it has checked that array formation of spacing of about 230nm and the perfect circle pore 20 like hole diameter 100nm was carried out.
[0066] (Example 2) In the production approach of the nano structure which anodizes aluminum film vapor-deposited on the substrate, and forms pore, this example formed the regular nano structure pattern which carried out the hexagonal-lattice array by performing two interference exposure to the resist formed on aluminum film, and this was used for it as an anodization mask. Hereafter, the production approach of the nano structure of this example is explained using drawing 6 R> 6.
[0067] (1) The aluminum film 31 (500nm of thickness) was first formed on the n-Si substrate 32 (drawing 6 (a)).
[0068] (2) After an acetone, washing by IPA, and desiccation, with the spin coat method, the resist film 33 (200nm of thickness) was applied, and it dried (drawing 6 (b)). (90-degree 20 minutes)
[0069] (3) Next, produce the regular nano structure pattern by the resist which carried out the hexagonal-lattice array periodically using interference exposure. In this example, helium-Cd laser

(lambda= 325nm, 230nm spacing of interference fringes) is used, and it is dose 14.75 mJ/cm2. 1st exposure was performed, as shown in drawing 7 , the resist 33 was exposed in the shape of a stripe, and the sensitization section 41 was formed. Then, the direction of an interference fringe is shifted 60 degrees from an interference fringe in the 1st interference exposure process, and it is exposure 14.75 mJ/cm2. It exposed. Then, in diluting a developer with pure water to 1 to 1, and developing it about 30 seconds with it, only the exposure intersection became a concave and the regular nano structure pattern which has the crevice 35 penetrated to the substrate front face was formed (drawing 6 (c)). Periodic spacing of the shape of a stripe in this example is 230nm, and as shown in drawing 8 , 34 is x(2/root3) 230**266nm in periodic spacing of an exposure intersection part.

[0070] (4) Next, it anodized by phosphoric-acid 0.3M solution and 130V (drawing 6 (d)).

[0071] (5) Finally, resist exfoliation liquid was used, the resist 31 was removed from the processed substrate, it was immersed in the 5wt% phosphoric acid for 30 minutes, puncturing processing (pore wide processing) was performed, and the pore 42 which carried out the hexagonal-lattice array periodically was formed (drawing 6 (e)).

[0072] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, as shown in drawing 9 , corresponding to the exposure intersection part, it has checked that array formation of spacing of about 266nm and the perfect circle pore 42 like hole diameter 100nm was carried out.

[0073] (Example 3) In the production approach of the nano structure which anodizes aluminum film vapor-deposited on the substrate, and forms pore, this example formed the regular nano structure pattern which carried out the four-way-type array by performing two interference exposure to the resist formed on aluminum film, and this was used for it as an anodization mask. Hereafter, the production approach of the nano structure of this example is explained using drawing 10 .

[0074] (1) The aluminum film 51 (500nm of thickness) was first formed on the n-Si substrate 52 (drawing 10 (a)).

[0075] (2) After an acetone, washing by IPA, and desiccation, with the spin coat method, the resist film 53 (200nm of thickness) was applied, and it dried (drawing 10 (b)). (90-degree 20 minutes)

[0076] (3) Next, produce the regular nano structure pattern by the resist which carried out the four-way-type array periodically using interference exposure. In this example, helium-Cd laser (lambda= 325nm, 230nm spacing of interference fringes) is used, and it is dose 14.75 mJ/cm2. 1st exposure was performed, as shown in drawing 11 , the resist 53 was exposed in the shape of a stripe, and the sensitization section 61 was formed. Then, the direction of an interference fringe is shifted 90 degrees from an interference fringe in the 1st interference exposure process, and it is exposure 14.75 mJ/cm2. It exposed. Then, in diluting a developer with pure water to 1 to 1, and developing it about 30 seconds with it, only the exposure intersection became a concave and the regular nano structure pattern which has the crevice 55 penetrated to the substrate front face was formed (drawing 10 (c)). Periodic spacing of the shape of a stripe in this example is 230nm, and as shown in drawing 12 , the periodic spacing 54 of an exposure intersection part is 230nm.

[0077] (4) Next, it anodized by phosphoric-acid 0.3M solution and 130V (drawing 10 (d)).

[0078] (5) Finally, resist exfoliation liquid was used, the resist 53 was removed from the processed substrate, it was immersed in the 5wt% phosphoric acid for 30 minutes, puncturing processing (pore wide processing) was performed, and the pore 62 which carried out the four-way-type array periodically was formed (drawing 10 (e)).

[0079] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, as shown in drawing 13 , corresponding to the exposure intersection part, it has checked that array formation of spacing of about 230nm and the perfect circle pore 62 like hole diameter 100nm was carried out.

[0080] (An example 4) After forming the regular nano structure pattern which used interference exposure for the resist and carried out the hexagonal-lattice array, the ion-milling exposure performed on the whole surface, it exfoliated, the antireflection film of a resist substrate pulled corresponding to the regular nano structure pattern, continuation anodic oxidation performed, and the regular nano structure

pattern which carried out the hexagonal-lattice array produced to a workpiece (an aluminum plate) in this example (in addition, it is producible also about the nano structure pattern which carried out the four-way-type array). Hereafter, the production approach of the nano structure of this example is explained using drawing 14 .

[0081] (1) The laminating of the antireflection film 72 and the resist film 73 was carried out on the aluminum plate 71, interference exposure was used for this, and the regular nano structure pattern by the resist in which the crevice 74 carried out the hexagonal-lattice array periodically was produced like the example 2 (drawing 1414 (a)).

[0082] (2) The ion milling exposure was performed all over the sample, and the antireflection film 72 of a resist substrate was exfoliated corresponding to the regular nano structure pattern (drawing 14 (b)).

[0083] (3) The resist 73 was removed with resist exfoliation liquid after anodization, the antireflection film 72 was removed with antireflection film exfoliation liquid, it was immersed in the 5wt% phosphoric acid for 30 minutes, and puncturing processing was performed (drawing 14 (c)).

[0084] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, it has checked that the spacing of about 266nm and the perfect circle pore 75 like hole diameter 100nm which carried out the hexagonal-lattice array periodically were formed.

[0085] (Example 5) In this example, after forming the regular nano structure pattern which used interference exposure for the resist formed on Si substrate, and carried out the four-way-type array, anodization was performed and the regular nano structure pattern which carried out the four-way-type array was produced to Si substrate (in addition, it is producible also about the nano structure pattern which carried out the hexagonal-lattice array.). Hereafter, the production approach of the nano structure of this example is explained using drawing 15 .

[0086] (1) The resist film 82 was formed on the Si substrate 81, interference exposure was used for this, and the regular nano structure pattern by the resist in which the crevice 83 carried out the four-way-type array periodically was produced like the example 3 (drawing 15 (a)).

[0087] (2) Anodization was performed in HF acid solution and the nano structure pattern by the resist which carried out the periodic four-way-type array was produced to the Si substrate 81 (drawing 15 (b)).

[0088] (3) Finally the resist 82 was exfoliated with resist exfoliation liquid (drawing 15 (c)).

[0089] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, it has checked that the perfect circle pore 84 with a spacing of about 230nm which carried out the four-way-type lattice periodically was formed.

[0090] (Example 6) In this example, the magnetic substance was embedded at the nano structure with periodic pore, and the magnetic device was produced. Hereafter, the production approach of the magnetic device of this example is explained using drawing 16 .

[0091] (1) The Pt film 92 (50nm of thickness) was first formed on the n-Si substrate 91 (drawing 16 (a)).

[0092] (2) Next, the aluminum film 93 (500nm of thickness) was formed on this Pt/n-Si (drawing 16 (b)).

[0093] (3) Next, after forming the resist film 94, the crevice 95 was formed in the resist film 94 by the same interference exposure as an example 2, and the regular nano structure pattern by the resist film 94 with periodic structure was produced (drawing 16 (c)). In addition, formation of this regular nano structure pattern can also be performed like an example 1 and examples 3-5.

[0094] (4) Next, it anodized by phosphoric-acid 0.3M solution and electrical-potential-difference 130V (drawing 16 (d)). At this time, anodic oxidation was completed with reduction of the current value in a current profile.

[0095] (5) Next, the resist film 94 was removed with resist exfoliation liquid, it was immersed in the 5wt% phosphoric acid for 30 minutes, and puncturing processing was performed (drawing 16 </A> (e)).

[0096] (6) Next, it was electrodeposited by soaking in Co electrodeposition liquid (drawing 16 (f)).

[0097] (7) Finally, diamond paste with a particle size of 500A was used, and flattening of the front face

was ground and carried out (drawing 16 (g)).
[0098] <Evaluation> The nano structure produced by the above-mentioned approach was observed by FESEM. Consequently, it has checked that Co was uniformly electrodeposited by the spacing of about 266nm and the perfect circle pore 96 like hole diameter 100nm which carried out the hexagonal-lattice array periodically.
[0099]
[Effect of the Invention] As explained above, there is the following effectiveness in this invention.
[0100] (1) By the manufacture approach of the nano structure of this invention forming a regular nano structure pattern on a workpiece using interference exposure, and anodizing a workpiece, the pore of the shape of a regular perfect circle can be formed over a large area, and it becomes possible to produce the nano structure (alumina pore) by which the pore of the shape of a perfect circle which was excellent in linearity over the whole region of patterning as the example has been arranged regularly. Moreover, the high nano structure of an aspect ratio is producible by performing anodization and anodic oxidation, using the regular nano structure pattern formed by interference exposure as a mask of a workpiece. Since especially interference exposure uses the interference wave of a sinusoidal component, it is conquerable that a high aspect ratio pattern cannot be minced to the resist itself.
[0101] (2) Moreover, since the manufacture approach of the nano structure of this invention uses the regular nano structure pattern for formation of a pore formation start point, putting a pressure on a workpiece, when forming a pore formation start point, positioning of a stamper, etc. are unnecessary, and a mechanical strength can apply them also to the workpiece which is not strong.
[0102] (3) Since it is possible to expose aluminum on a front face also to a workpiece by which the film was formed in aluminum front face if it is less than the thickness (difference of elevation) of a nano structure pattern since the regular nano structure pattern is used for formation of a pore formation start point, the manufacture approach of the nano structure of this invention can still form a pore formation start point.
[0103] (4) Since the manufacture approach of the nano structure of this invention uses a regular nano structure pattern, only depending on the concave location of nano structure, random-arrangement-izing of pore is still more possible for a pore formation start point. Moreover, in anodic oxidation, in order that pore may grow by the shape of a perfect circle, the penetration part of periodic nano structure may not be a perfect circle.
[0104] (5) In two points of point ** which does not have to carry out direct patterning to a workpiece front face far by the large area, the point which can produce the periodic nano structure by low cost, electron beam lithography, etc., and does not damage a workpiece, it is more practical than using semi-conductor processing techniques, such as X-ray lithography and electron beam lithography, further.
[0105] (6) Moreover, this invention makes it possible to apply the pore object of an anodic oxidation alumina with various gestalten, and extends the application range remarkably. Furthermore, the nano structure of this invention can also be used as the base material of the further new nano structure, mold, etc., although it is usable as a functional material in itself.

[Translation done.]

* NOTICES *

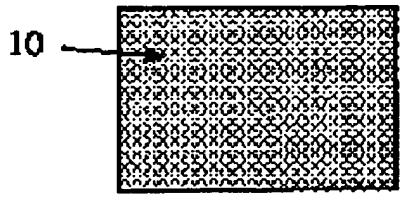
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing for explaining 1 operation gestalt of the manufacture approach of the nano structure of this invention.
[Drawing 2] It is drawing for explaining 1 operation gestalt of the manufacture approach of the nano structure of this invention.
[Drawing 3] It is a sectional view for explaining the manufacture approach of the nano structure concerning the example 1 of this invention.
[Drawing 4] It is the top view showing the regular nano structure pattern concerning the example 1 of this invention.
[Drawing 5] It is the top view showing the nano structure manufactured in the example 1 of this invention.
[Drawing 6] It is a sectional view for explaining the manufacture approach of the nano structure concerning the example 2 of this invention.
[Drawing 7] It is the top view showing the 1st interference exposure pattern in the manufacture approach of the nano structure concerning the example 2 of this invention.
[Drawing 8] It is the top view showing the regular nano structure pattern concerning the example 2 of this invention.
[Drawing 9] It is the top view showing the nano structure manufactured in the example 2 of this invention.
[Drawing 10] It is a sectional view for explaining the manufacture approach of the nano structure concerning the example 3 of this invention.
[Drawing 11] It is the top view showing the 1st interference exposure pattern in the manufacture approach of the nano structure concerning the example 3 of this invention.
[Drawing 12] It is the top view showing the regular nano structure pattern concerning the example 3 of this invention.
[Drawing 13] It is the top view showing the nano structure manufactured in the example 3 of this invention.
[Drawing 14] It is the top view and sectional view for explaining the manufacture approach of the nano structure concerning the example 4 of this invention.
[Drawing 15] It is the top view and sectional view for explaining the manufacture approach of the nano structure concerning the example 5 of this invention.
[Drawing 16] It is a sectional view for explaining the manufacture approach of the magnetic device concerning the example 6 of this invention.
[Description of Notations]
10 Aluminum Plate
11 Aluminum Film
11' Alumina film
12 N-Si Substrate

13 Resist
14 Periodic Spacing of the Shape of a Stripe in 1st Interference Exposure
15 Antireflection Film
16 Part of Resist Exposed in the shape of SUTORAIBU
17 Part Penetrated to Concave to Workpiece (Aluminum Film) after Developing Exposure Intersection Part of Interference Exposure Covering 2 Times
18 Spacing of Pore Which Carried Out Hexagonal-Lattice Array
19 Regular Pore Formed in Aluminum Film of Anodic Oxidation
20 Regular Pore Which Performed Puncturing Processing
31 Aluminum Film
31' Alumina film
32 N-Si Substrate
33 Resist Film
34 Spacing of Pore Which Carried Out Hexagonal-Lattice Array
35 Part Penetrated to Concave to Workpiece after Developing Exposure Intersection Part of Interference Exposure Covering 2 Times
41 Resist Exposed in the shape of a Stripe
42 What Carried Out Puncturing Processing of the Pore Which was Formed in Aluminum Film of Anodic Oxidation, and Which Carried Out Hexagonal-Lattice Array
51 Aluminum Film
51' Alumina film
52 N-Si Substrate
53 Resist Film
54 Spacing of Pore Which Carried Out Four-Way-Type Array Periodically
55 Part Penetrated to Concave to Workpiece after Developing Exposure Intersection Part of Interference Exposure Covering 2 Times
61 Resist Part Exposed in the shape of a Stripe
62 What Carried Out Puncturing Processing of the Pore Which was Formed in Aluminum Film of Anodic Oxidation, and Which Carried Out Periodic Four-Way-Type Array
71 Aluminum Plate
72 Antireflection Film 73 Resist
74 Resist Pattern Which was Formed of Interference Exposure Covering 2 Times and Which Carried Out Hexagonal-Lattice Array Periodically
75 Pore Formed in Workpiece (Aluminum Plate) of Anodic Oxidation
81 Si Substrate
82 Resist
83 Resist Pattern Which was Formed of Interference Exposure Covering 2 Times and Which Carried Out Four-Way-Type Array Periodically
84 Pore of Workpiece (Si) Formed of Anodization
91 Si Substrate
92 Pt Film
93 Aluminum Film
93' Alumina film
94 Resist
95 Part Penetrated to Concave to Workpiece after Developing Exposure Intersection Part of Interference Exposure Covering 2 Times
96 What Carried Out Puncturing Processing of the Pore Which was Formed in Aluminum Film of Anodic Oxidation, and Which Carried Out Hexagonal-Lattice Array
97 Co Electrodeposited in Pore

(a)



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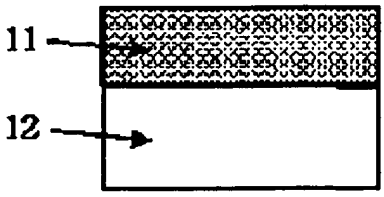

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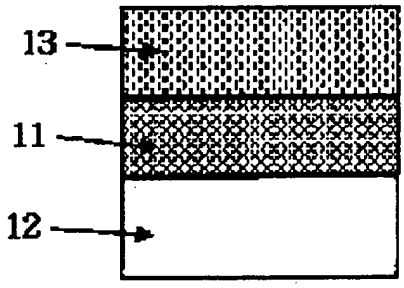

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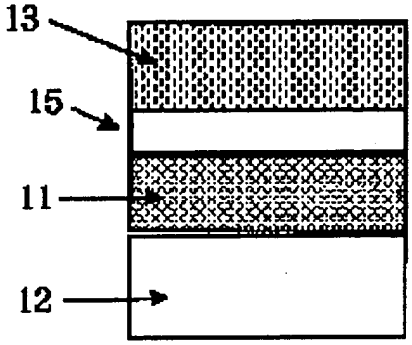

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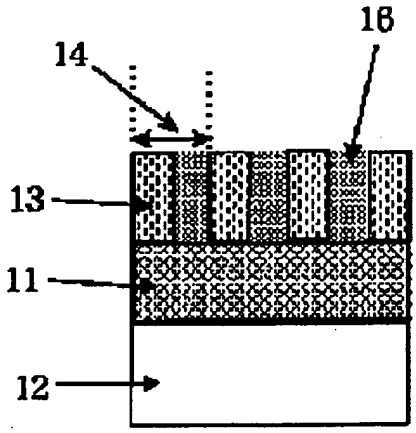

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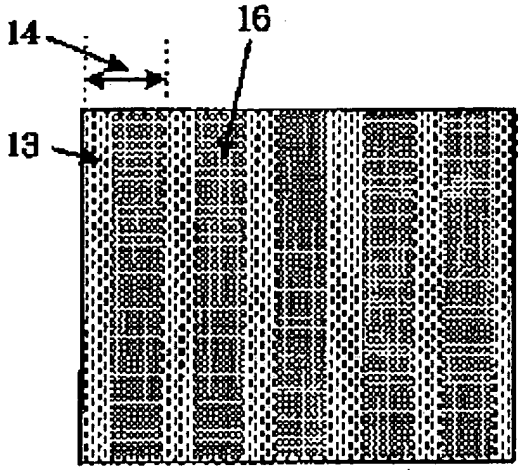

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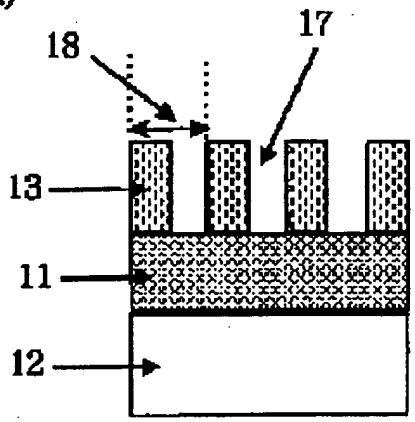

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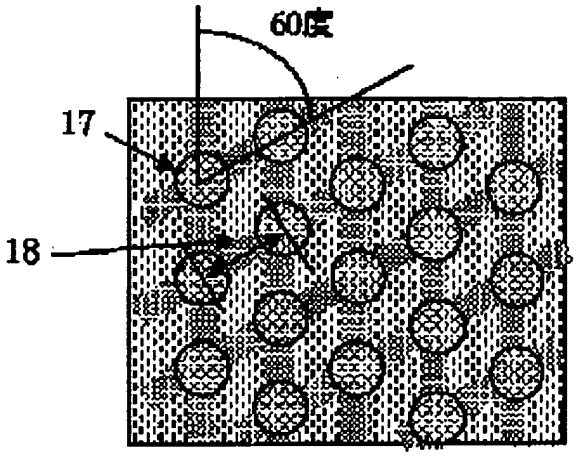

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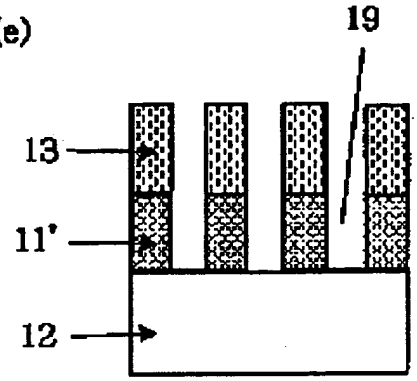

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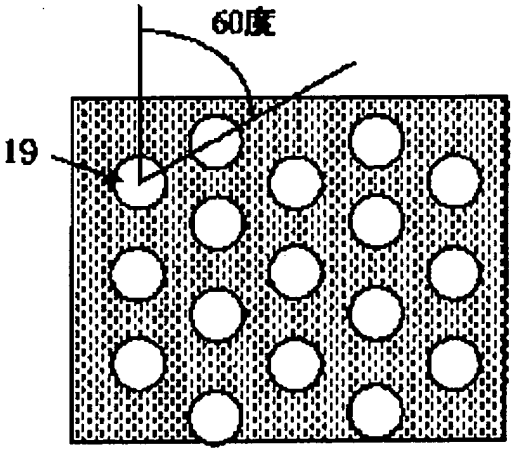

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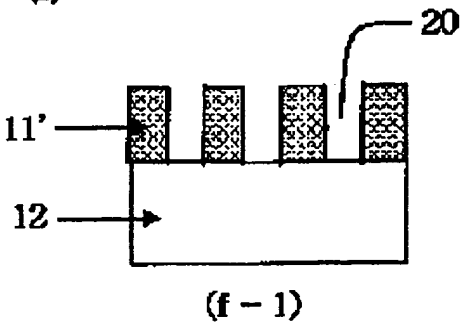

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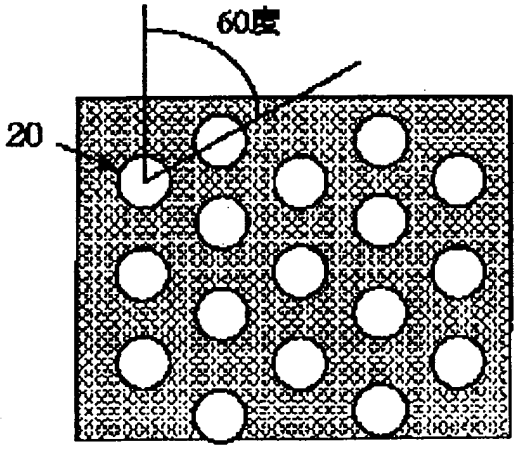

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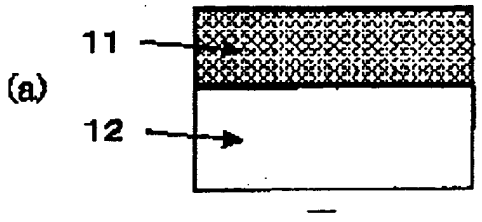
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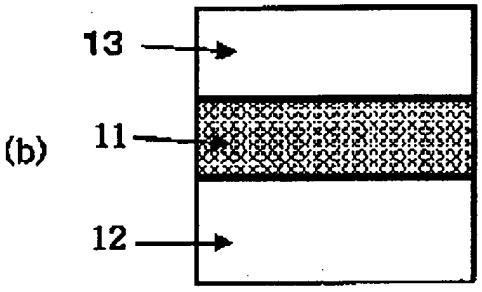
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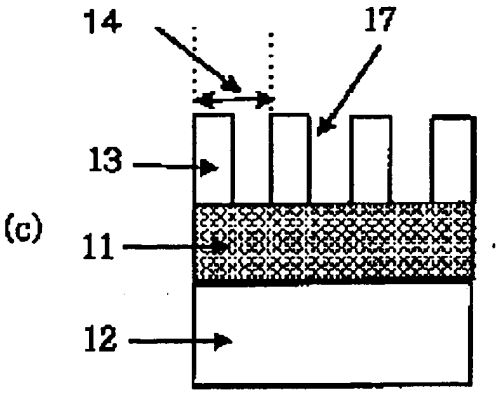
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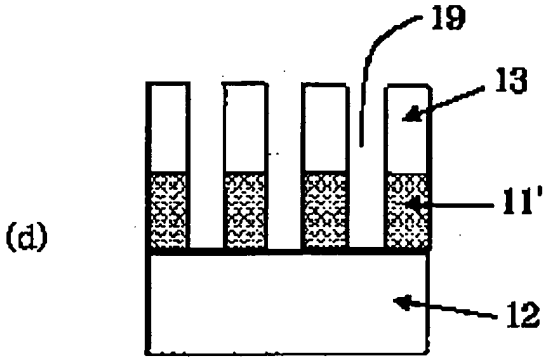
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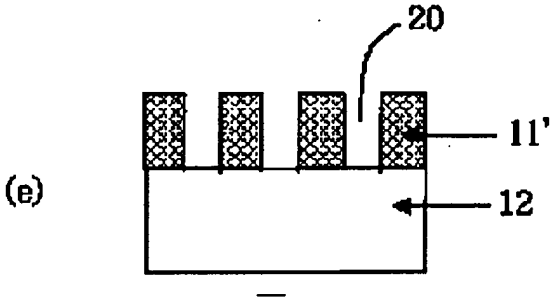
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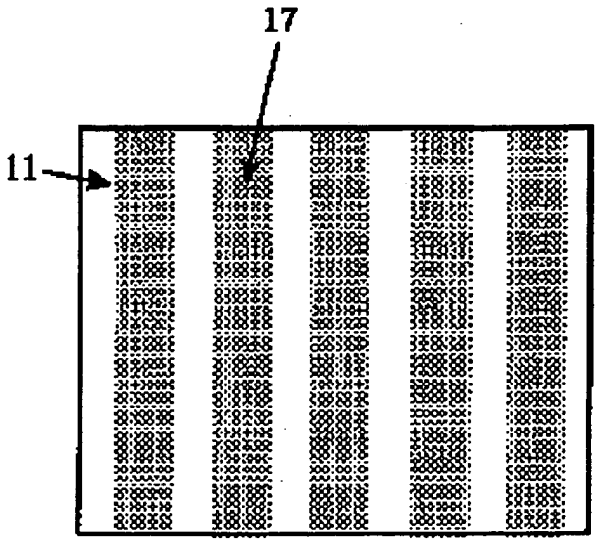
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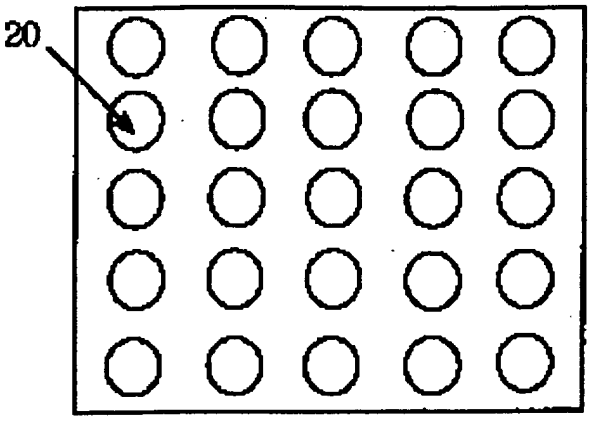
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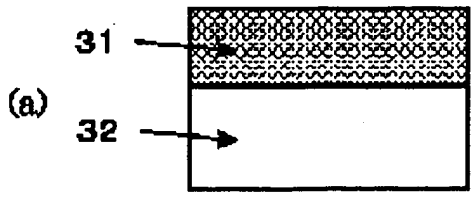
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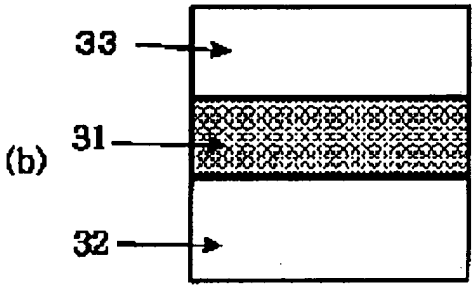
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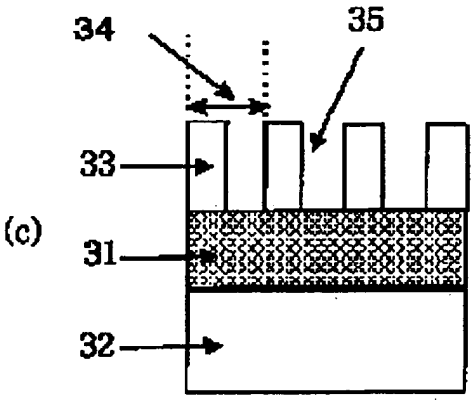
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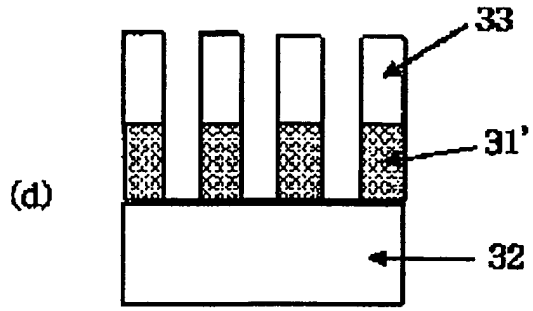
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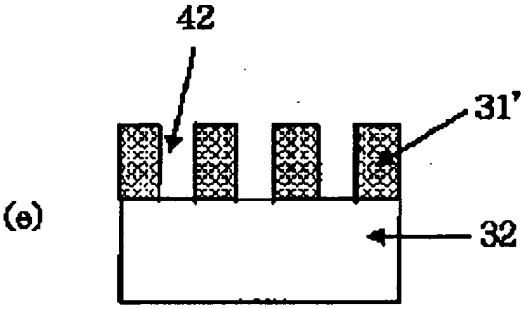
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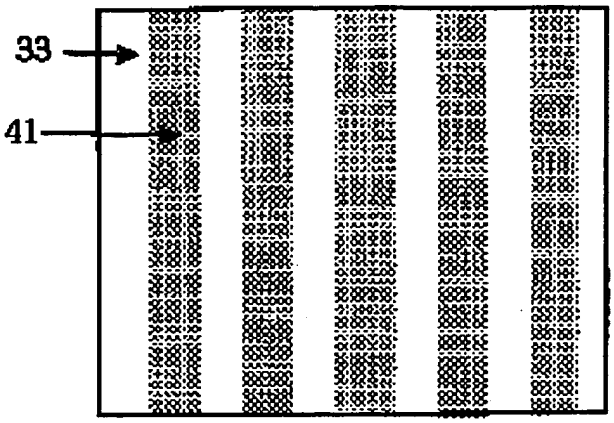
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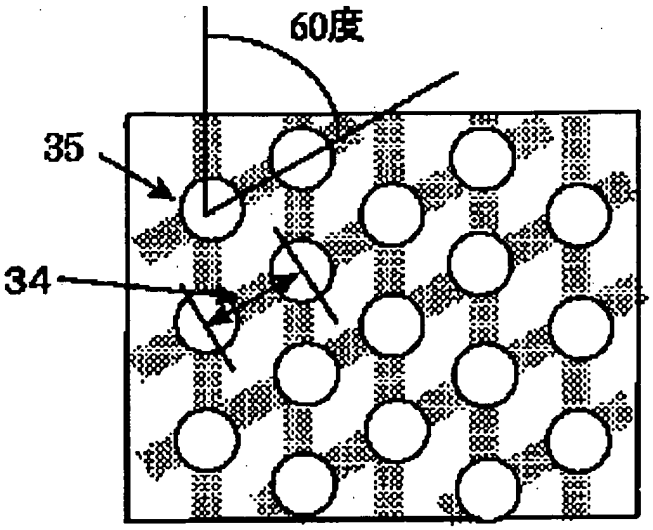
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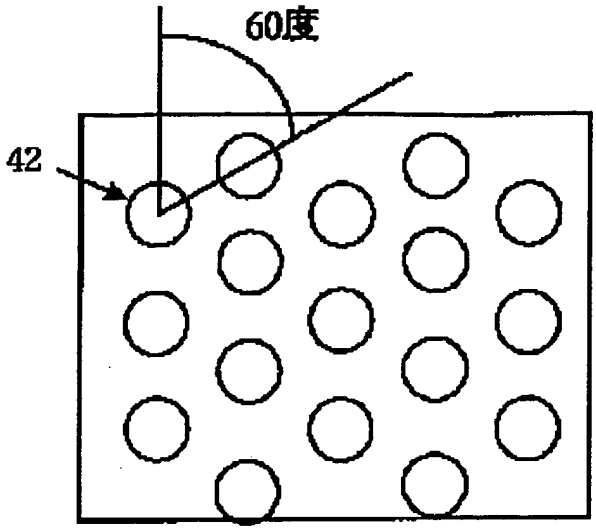
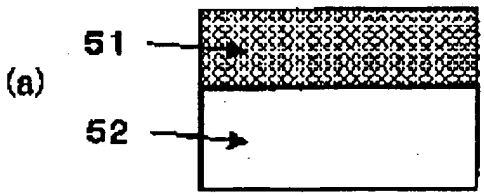
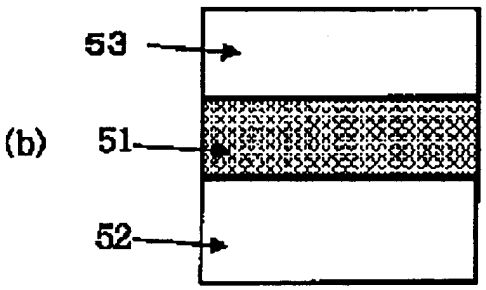
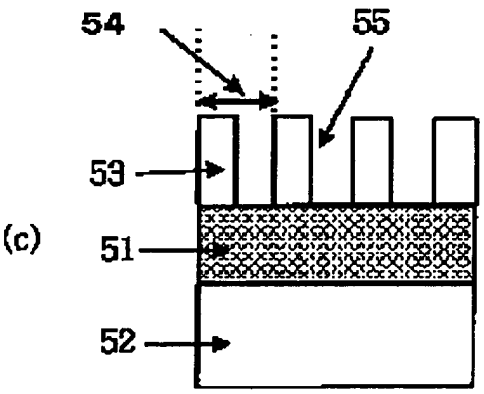
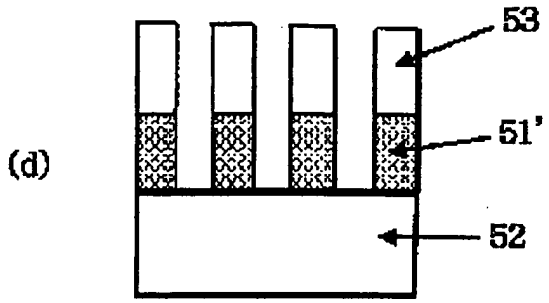
35
34

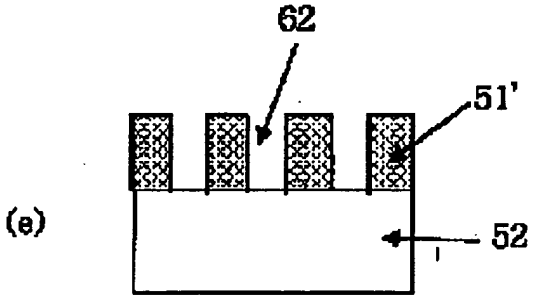

60度
42

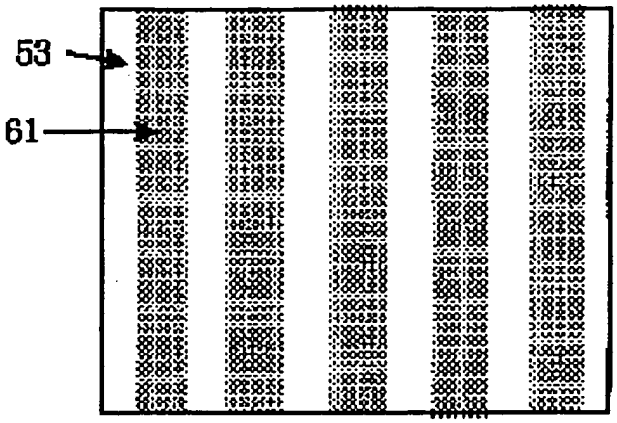

(a)
51
52

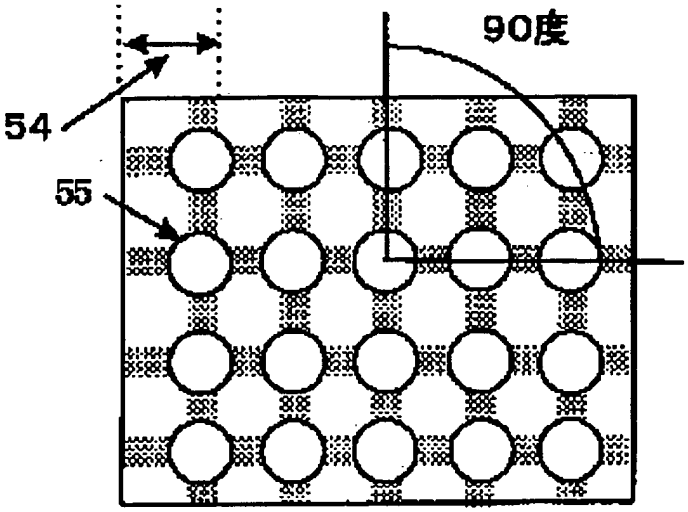

(b)
53
51
52

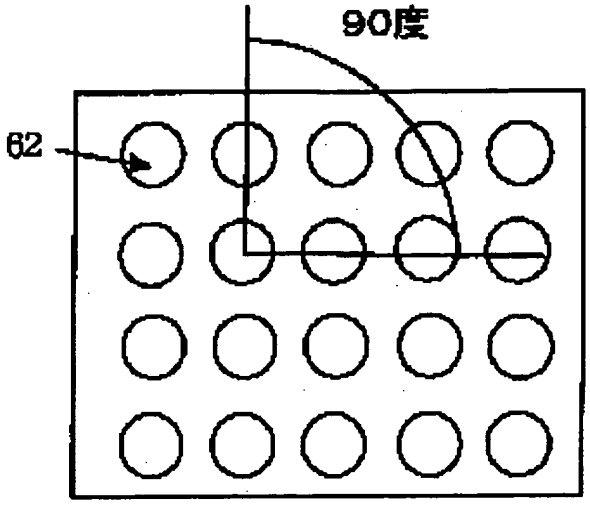

(c)
54
55
53
51
52

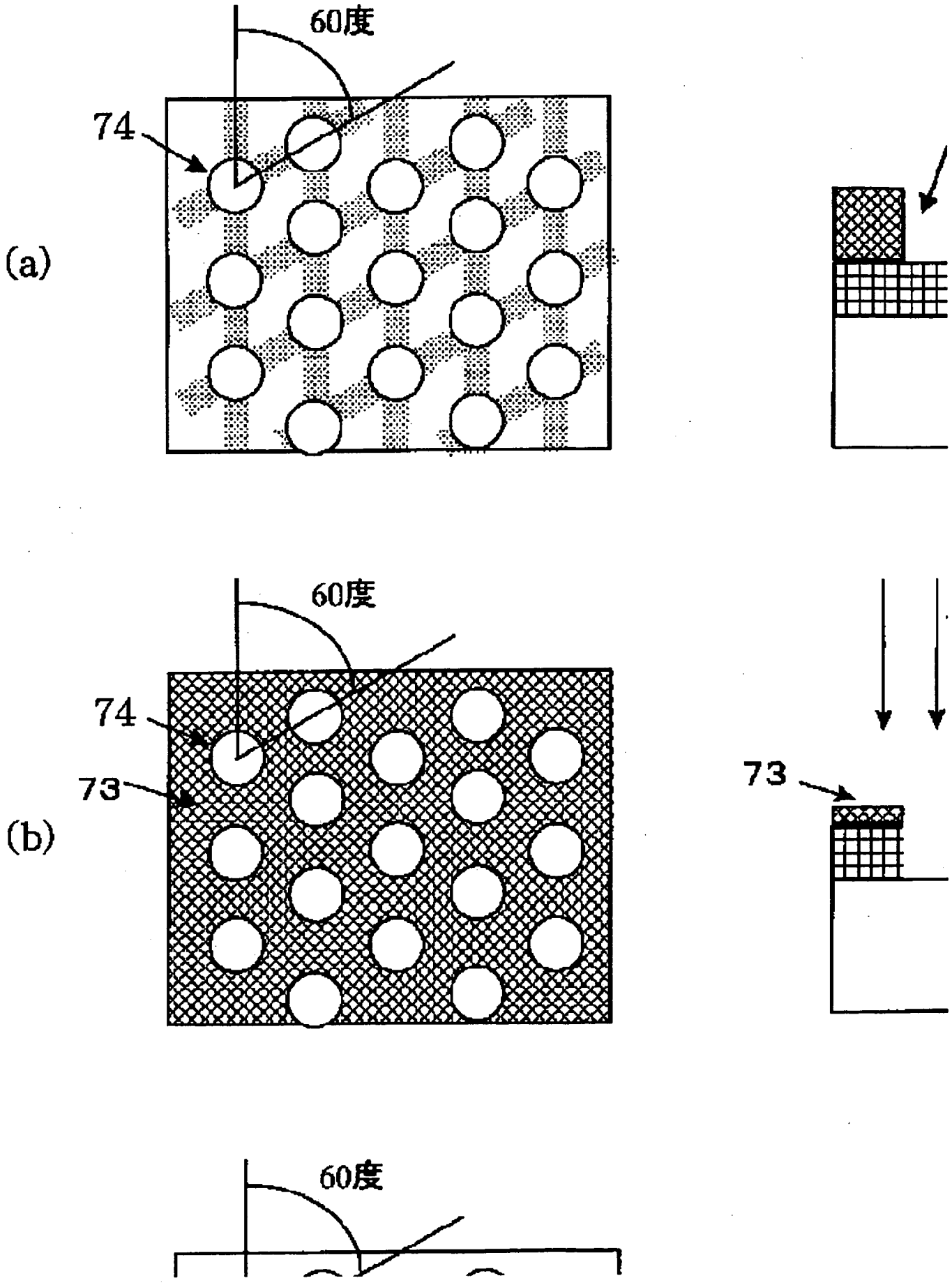

(d)
53
51'
52


(e)
62
51'
52

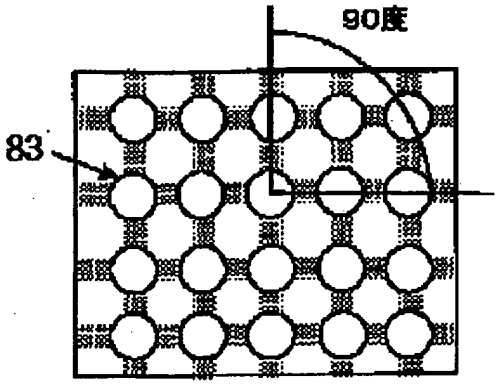

53
61

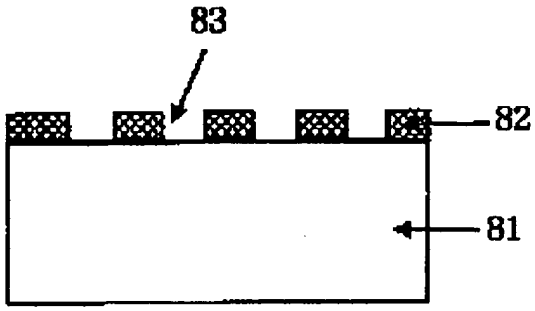

90度
54
55


90度
62

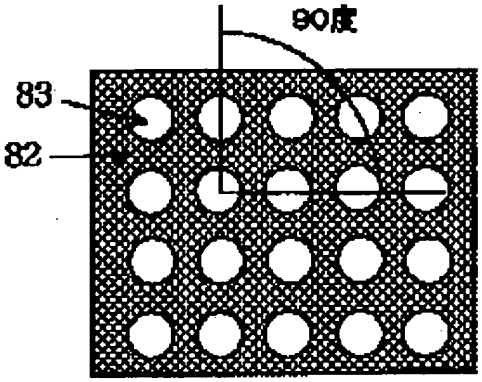

60度
74
(a)
60度
74
73
(b)
73
60度

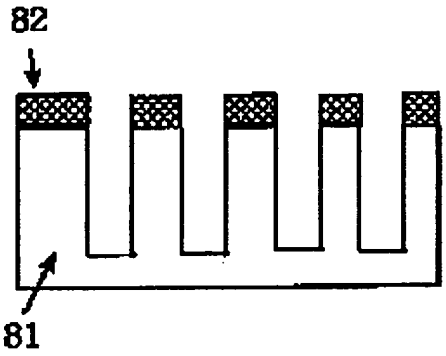
(a)



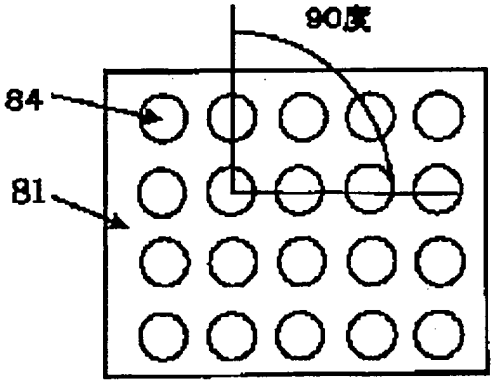


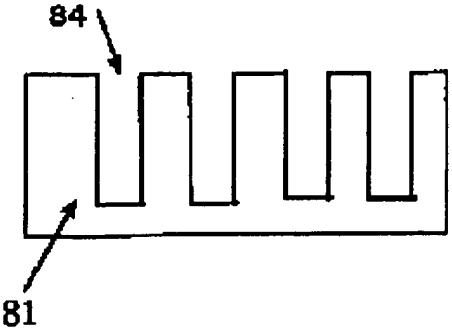
(b)

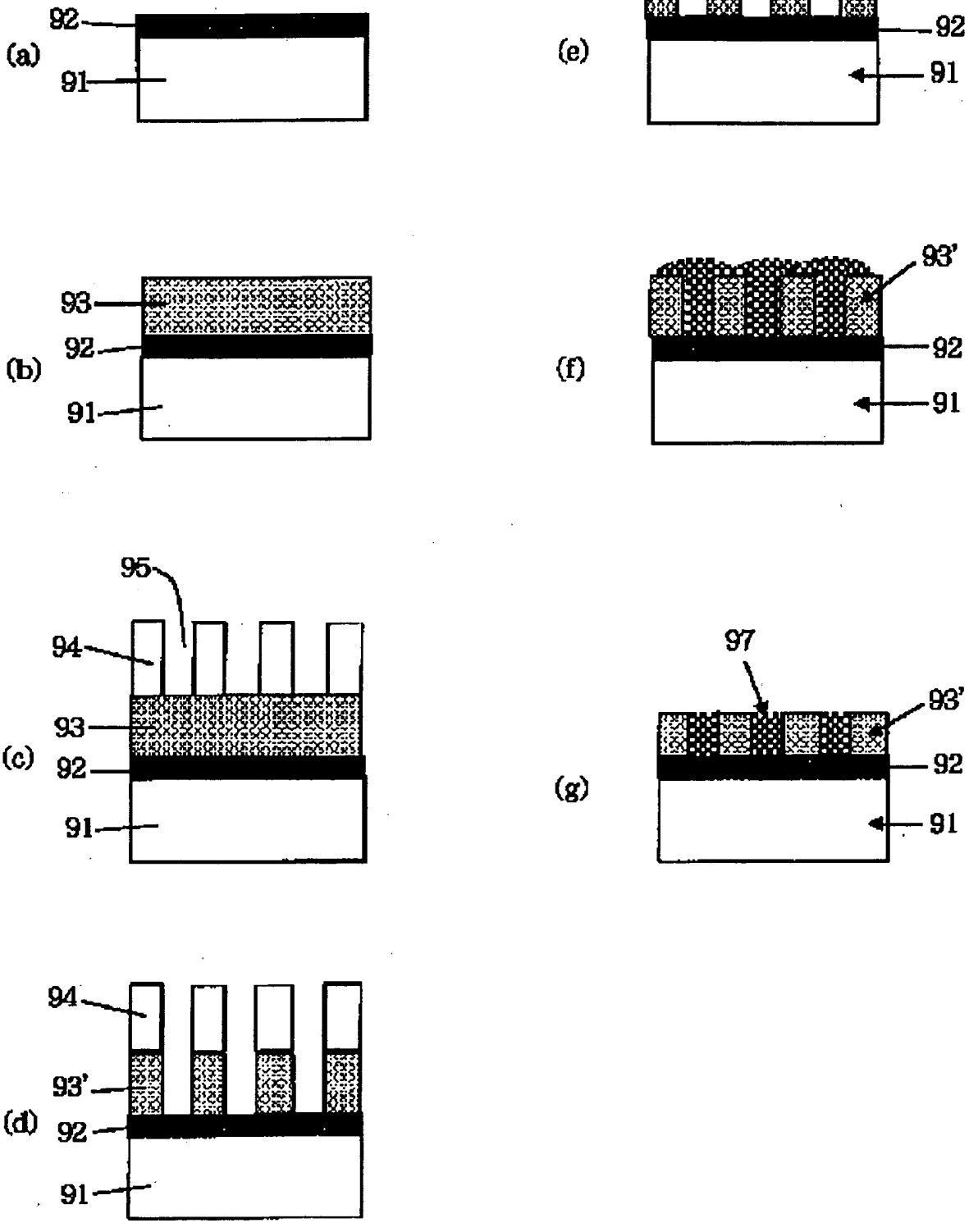




(c)






(a)
92
91
(b)
93
92
91
(c)
95
94
93
92
91
(d)
94
93'
92
91
(e)
96
93'
92
91
(f)
93'
92
91
(g)
97
93'
92
91